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NATIONAL BUREAU OF STANDARDS REPORT

6111

THERMAL AND SELF-IGNITION PROPERTIES OF THREE SOLID PROPELLANTS

by

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and

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U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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Thermal and Self-Ignition Properties of Three Solid Propellants

J. J. Loftus and D. Gross

ABSTRACT

Measurements have been made of the specific heat, thermal conductivity and kinetic properties of three solid propellants. Based upon these measurements, estimates are provided of the self-ignition hazard associated with the use and bulk storage of such propellants.

INTRODUCTION

An understanding of the mechanism of the thermal decomposition of explosives, propellants, and fuels requires knowledge of the kinetics of the reactions involved. One application of this knowledge is in the analysis of the self-ignition hazard associated with the use or storage of these materials. With the present trend toward the design and use of large rocket propellant grains, basic information on the size limitations for storage of such propellants is important.

At the request of the Naval Ordnance Laboratory, letter dated 12/23/57, s/G. K. Hartman, determination of the thermal and kinetic properties of several solid propellants was initiated. Based upon an analysis of the self-heating reaction and the magnitude of these properties, an estimation may be made of the critical size and temperature conditions for self-ignition.

MATERIALS

The three solid propellant materials were furnished by the Naval Ordnance Laboratory in the shapes required for test and were identified as A, B and C in the chronological order of their receipt.

EXPERIMENTAL WORK

A. Thermal Conductivity Measurements

For these measurements, a heat-flow meter type of thermal conductivity apparatus[1] was used. In operation, two slabs each 10 by 10 by 1-in., comprising a sample pair of the specimen under test are placed one on each side of a heat-flow meter and then the faces of a hot plate and of a cold plate are brought together to make intimate contact with the specimens. At steady state, the heat flowing through the meter from the hot plate maintained at 32.8°C (91°F) to the cold plate maintained at 13.3°C (56°F) produces an emf proportional to the temperature gradient through the meter. The coefficient of thermal conductivity for each specimen was determined from the heat-flow meter output, the thickness of the specimen and the temperature drop in the specimen as measured by thermocouples. The heat-flow meter was calibrated by tests made on two materials of known conductivities as previously determined using a guarded hot plate (ASTM C 177-45). Two tests, one "forward" and one "reverse", were performed on propellants A and B. Since only one 10 by 10 by 1-in. specimen of propellant C was available for test, this propellant was tested in only one direction.

The results are summarized in Table 1.

Table 1. Thermal Conductivity Measurements

Material	Density g/cm^3	Mean Temperature °C	Thermal Conductivity cal/sec-cm-deg C	
Propellant A	1.621	23.1	0.0005253 0.0005315	0.000527±1%
Propellant B	1.786	23.1	0.001322 0.001329	0.001326±0.5%
Propellant C	1.634	31.0		0.001002±1%

B. Specific Heat Measurements

For these measurements, each propellant sample measured 1 by 2 by 2-1/2-in. To eliminate the possibility of interaction between the propellants and the water bath of the calorimeter, propellants A and B were sealed in individual plastic envelopes while propellant C was spray-coated with a plastic film for test. The specific heats of the samples were measured by substituting them, separately, for 100 g of water in a calorimeter normally containing 600 g, and measuring the energy equivalent of the calorimeter and contents electrically. From the value obtained for the calorimeter with 600 g of water and the values obtained when the propellants were tested, the specific heats of the propellants including their plastic envelopes were obtained. The specific heat of the propellant was determined using a value of 0.69 cal/g-deg C for the specific heat of the plastic envelope. The specific heat of water was taken as 0.99921 cal/g at 22.5°C. Measurements were made over a 3 to 4 deg C range between 20 and 25°C. This method of measurement groups all the errors of measurement into the value obtained for the specific heat of the propellant. Two duplicate tests on the same sample were performed and the results are summarized in Table 2.

Table 2. Specific Heat Measurements

Material	Sample Weight g	Envelope Weight g	Temp. Rise deg C	Mean Temp. °C	Specific Heat cal/g-deg C	
Propellant A	134.1903	1.8603	3.337	23.2	0.3906	
			3.325	22.3	0.3731	0.38±0.01
Propellant B	145.5787	1.7949	3.841	22.9	0.2827	
			3.500	23.0	0.3026	0.29±0.01
Propellant C	140.9178	4.3152*	3.163	23.4	0.3124	
			3.234	23.5	0.2925	0.30±0.01

*sprayed-on plastic film

C. Kinetic Measurements

For these measurements, two pre-cut wafers 2-in. in diameter by 1-in. thick as furnished were placed together to form a cylindrical specimen 2-in. in diameter by 2-in. long.

The specimen was assembled and mounted within a furnace designed for self-heating studies.[2] During the initial heating period, the thermostatically controlled furnace air temperature was gradually increased by small temperature intervals. At a temperature at which an indication of self-heating was obtained according to the signal from a differential thermopile, the control system was actuated to provide "adiabatic" or compensating temperature rise control. The differential thermopile was composed of four (4) 28 ga. (B & S) chromel-alumel thermocouples in series to indicate the mean temperature difference between the specimen and the furnace atmosphere. The electrical signal from the differential thermopile was applied to an amplifier and servo control system so as to automatically compensate for any temperature rise within the specimen. Under these conditions, the specimen temperature remains uniform throughout its mass and the heat generated within the body increases its temperature according to the relation:

$$c\rho dT/dt = A\epsilon^{-E/RT} \qquad (1)$$

where T = absolute temperature, K
t = time, sec
ρ = specimen density, g/cm^3
c = specific heat, cal/g-deg C
A = heat generation coefficient, cal/sec-cm^3
E = activation energy, kcal/mole
R = gas constant = 0.001987 kcal/mole- K

Continuous records, Figures 1, 2, and 3*, of the specimen and furnace air temperatures were obtained on an automatic recorder from the signals of 24 ga. (B & S) chromel-alumel thermocouples. Measurements were made of the slope of the curve, dT/dt, at a number of temperatures over the self-heating range. By taking logarithms and plotting ln dT/dt versus 1/T, the resultant line has a slope of -E/R, and intercepts the ln dT/dt axis at ln A/ρ c. At least two tests for each propellant were performed and the results from one test for each propellant is shown in Figure 4 together with those from similar tests on nitrocellulose plastic, wood fiberboard and purified cotton linters.

*These records were only included in 5 copies of this report including those forwarded to the sponsor.

The plotted points approximate straight lines very closely and show the rate of temperature rise due to self-heating for each material under negligible heat loss conditions. Within the range shown, the displacement of a line toward higher values of reciprocal temperature indicates self-heating at relatively lower temperatures. Comparative rates of self-heating at any temperature may be read directly from the graph as illustrated in Table 3.

Table 3. Comparative Rates of Self-Heating

Material	Rate of self-heating, deg C/min Temperature: 135°C (1/T = 0.002450)	Temperature: 209°C (1/T = 0.002075)
Propellant A	1.15	c
Propellant B	a	0.84
Propellant C	0.07	1.58
Nitrocellulose plastic	0.225	c
Wood fiberboard	0.025	2.3
Cotton linters	b	0.067

a. No appreciable self-heating until 190°C
b. No appreciable self-heating until 180°C
c. Specimen consumed

At 135°C, propellant A exhibited self-heating at a rate of 1.15 deg C/min, approximately 5 times that of nitrocellulose plastic and 50 times that of wood fiberboard, while propellant B exhibited no appreciable self-heating at temperatures below 190°C. At this same temperature, propellant C self-heated at a rate of 0.07 deg C/min. At 209°C, propellant A had been entirely consumed while propellant B exhibited self-heating at a rate of 0.84 deg C/min, approximately 1/3 that of wood fiberboard, and propellant C showed self-heating at a rate of 1.58 deg C/min, approximately 2/3 that of wood fiberboard.

The values of the kinetic constants determined from the lines in Figure 4 are listed in Table 4 for the applicable temperature ranges.

Table 4. Kinetic Measurements

Material	Temperature Ranges C	Activation Energy E kcal/mole	Heat Generation Coefficient A cal/sec-cm^3
Propellant A	100 - 170	38.8	6.99×10^{18}
Propellant B	190 - 242	49.3	1.56×10^{20}
Propellant C	165 - 235	28.6	1.17×10^{11}
Nitrocellulose plastic	134 - 169	42.0	2.43×10^{19}
Wood fiberboard	80 - 225	25.7	1.97×10^{9}
Cotton linters	180 - 260	34.5	5.30×10^{11}

In the tests with propellants B and C, a (nearly) constant temperature phase was observed at a temperature of about 240°C. One possible explanation for this behavior would be a change in crystal structure occurring at this temperature.

In the tests with propellant C, melting, softening or slumping of the propellant was observed at a temperature of about 140 to 160°C. For the purposes of this analysis, it was assumed that the self-heating characteristics of the melted or slumped propellant were the same as those of the original solid.

Due to the unexpected behavior of propellant C in the first few tests, a total of six tests were performed on specimens of this material and details of each of the tests are described below.

Test No. 1

At an initial temperature setting of 114°C, no appreciable self-heating was observed. After 38 minutes at this temperature, the temperature was raised to 156°C. The specimen self-heated to 243°C in 65 minutes and remained at this temperature for about 2 minutes. After this short constant-temperature

phase, very rapid combustion set in and the specimen was consumed. Based upon the data from this test, an activation energy of about 55 kcal/mole was computed.

Test No. 2

At an initial temperature setting of 141°C, very little self-heating was observed. After 136 minutes at this temperature, the temperature was raised to 149°C. The specimen self-heated to 162°C in 135 minutes at which time the adiabatic control operation and consequently the temperature measurements became erratic. It is interesting to note the behavior of this test specimen after the furnace temperature was increased in an effort to destroy the specimen. At a temperature of about 195°C, this decision was reconsidered and the furnace heater was turned off. The specimen continued to heat reaching a temperature of 225°C before it started to cool. It had cooled down to 215°C and was continuing to cool when recording was discontinued for the day. It was found on the next day that the specimen had been consumed.

Test No. 3

After 25 minutes at a temperature setting of 82°C, the furnace temperature was raised to 142°C. After 15 minutes, the adiabatic control operation became erratic as in Test No. 2. The test was discontinued after approximately 90 minutes during which period the maximum recorded specimen temperature was 147°C. The furnace and specimen were allowed to cool over night. Inspection of the furnace chamber the following day showed that the specimen had melted away from its holder and from the recording and controlling thermocouples and was found resolidified at the bottom of the furnace chamber.

On the basis of this finding, it was assumed that softening or melting had occurred in each of the previous tests. It is speculated that in Test No. 1 a small quantity of propellant material had remained in contact with the control thermopile to permit adiabatic control operation whereas in Test Nos. 2 and 3, complete separation had occurred. For all succeeding tests, the cylindrical propellant specimens were placed in a 2-in. diameter by 2-in. high stainless steel wire basket consisting of 40 mesh, 0.010-in. diameter wires. This basket served to support the softened or melting propellant specimen in position during the self-heating process.

Test No. 4

From an initial temperature of 130°C, the specimen self-heated to 238°C in about 15 hours. After a short pause at this temperature, very rapid combustion occurred and the specimen was consumed. The data on the rate of temperature rise versus reciprocal temperature for this test was best approximated by two straight lines yielding an activation energy of 38.1 kcal/mole for the temperature range 180 to 200°C and an activation energy of 19.9 kcal/mole for the temperature range 200 to 235°C.

Test No. 5

From an initial temperature of 130°C, the specimen self-heated to 238°C in about 12 hours. After a short delay at this temperature, very rapid combustion occurred and the specimen was consumed. Analysis of the data yielded an activation energy of 24.1 kcal/mole for this test.

Test No. 6

From an initial temperature of 131°C, the specimen self-heated to 236°C in about 10 hours. Following the characteristic pause at almost constant temperature, very rapid combustion occurred and the specimen was consumed. The activation energy for this test was calculated as 28.6 kcal/mole and is the value reported in the tables.

CALCULATION OF CRITICAL SIZE

In order to estimate the critical size for ignition of a mass of self-heating material, the analysis presented by Enig, Shanks and Southworth[3] was used. This relates the half-thickness of a material of given thermal and kinetic properties with the temperatures at the center and the surface under critical steady-state conditions. This analysis has been applied to wood fiberboard and cotton linters and fair agreement with experimental results has been obtained.[4]

The assumption was made that the kinetic properties measured over higher temperature ranges may be applied to the temperature range of practical interest for ordinary storage (20 - 100°C). It was further assumed that the measured thermal properties may be applied over the whole

temperature range. Critical radius determinations for a sphere have been made for each propellant and for three other common materials, and these are listed in Table 5 and shown graphically in Figure 5. It may be noted from the tables in reference 3 that for a given surface temperature, the critical radius for a cylinder and the critical half thickness for a semi-infinite slab are given very closely by 0.775 B_c and 0.514 B_c respectively, where B_c is the critical radius for the sphere.

Table 5. Critical Size Calculations

Material	Surface Temp.	Critical Radius of a Sphere 20°C (68°F)	48.9°C (120°F)	82.2°C (180°F)	100°C (212°F)
Propellant A		9800 cm 320 ft	540 cm 18 ft	35 cm 1.2 ft	10 cm 0.33 ft
Propellant B		2.4×10^7 7.9×10^5	6.0×10^5 2.0×10^4	1.8×10^4 580	3500 120
Propellant C		1.9×10^4 633	2351 77	318 10.4	128 4.2
Nitrocellulose plastic		7.7×10^4 2500	3300 110	170 5.5	43 1.4
Wood fiberboard		4500 150	680 22	110 3.7	50 1.6
Cotton linters		4.2×10^6 1.4×10^5	3.3×10^5 1.1×10^4	2.9×10^4 940	9400 310

SUMMARY

Measurements of the specific heat, thermal conductivity and kinetic properties of 3 propellants have been made.

In the self-heating experiments, propellant A self-heated from an initial temperature of 100°C to a temperature of 170°C in 10 hours. At this temperature, very rapid combustion occurred and the sample was consumed. The activation energy for propellant A over this temperature range was 38.8 kcal/mole. Propellant B self-heated in 2-1/2 hours from an initial

temperature of 190°C to a temperature of 242°C, at which temperature very rapid combustion occurred and the sample was consumed. The activation energy of propellant B over this temperature range was 49.3 kcal/mole. Propellant C self-heated in 10 hours from an initial temperature of 131°C to a temperature of 236°C at which temperature very rapid combustion occurred and the sample was consumed. The activation energy of propellant C over this temperature range was 28.6 kcal/mole.

A comparison of critical radius determinations, under the given assumptions, is presented in Table 5 and Figure 5. Size limitations on the storage of bulk quantities of propellant A, propellant C and nitrocellulose plastic, and careful control of temperature and ventilation conditions seem justified on the basis of these calculations. Although wood fiberboard is not normally considered a storage hazard at temperatures up to 60°C (140°F), it has been known to self-heat to ignition when stacked hot after drying during the manufacturing process. Propellant B does not appear likely to present any storage hazard with respect to self-ignition at ordinary storage temperatures.

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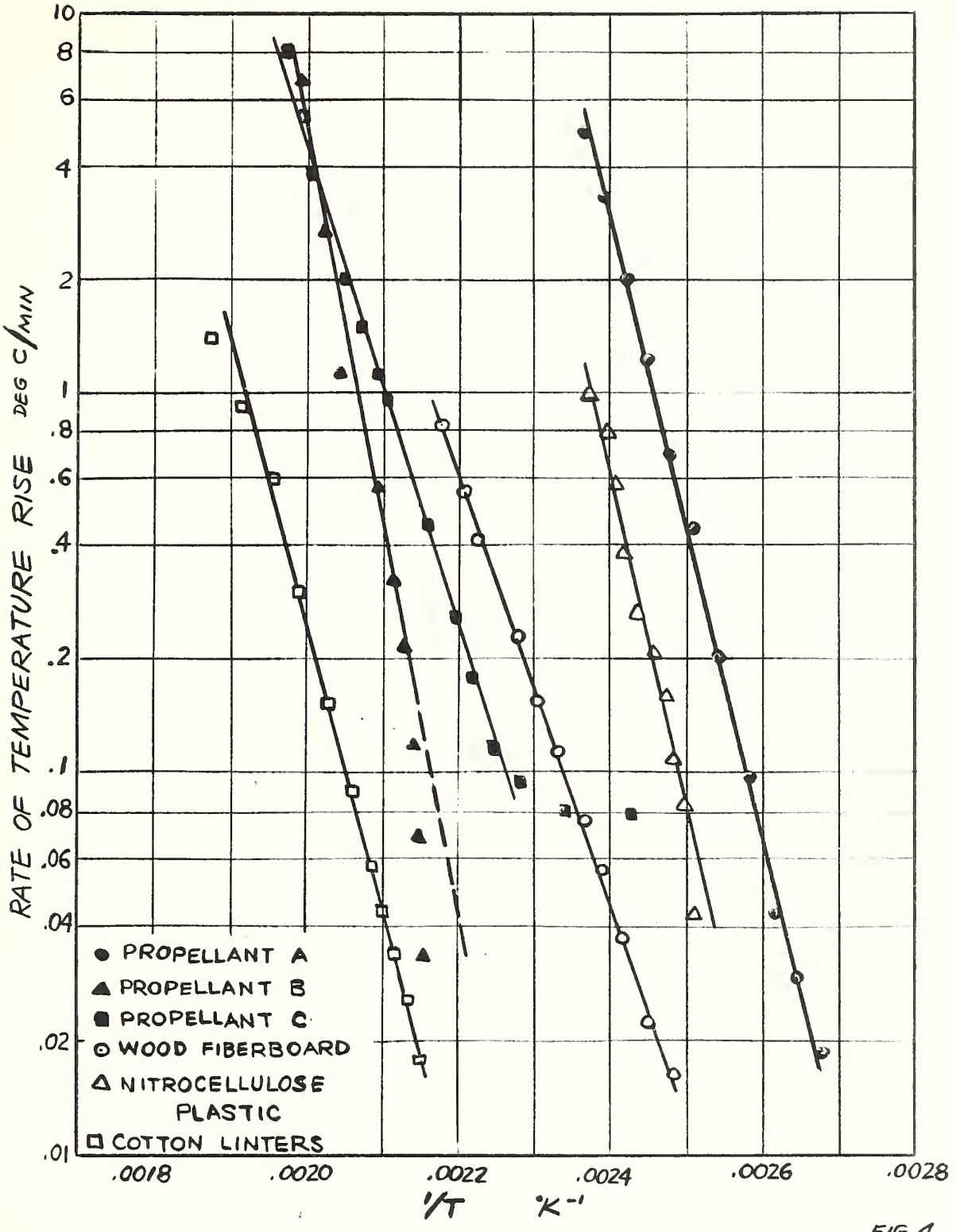
RATE OF TEMPERATURE RISE DEG C/MIN
10
8
6
4
2
1
.8
.6
.4
.2
.1
.08
.06
.04
.02
.01
PROPELLANT A
PROPELLANT B
PROPELLANT C
WOOD FIBERBOARD
NITROCELLULOSE PLASTIC
COTTON LINTERS
.0018
.0020
.0022
.0024
.0026
.0028
1/T °K⁻¹

FIG. 4

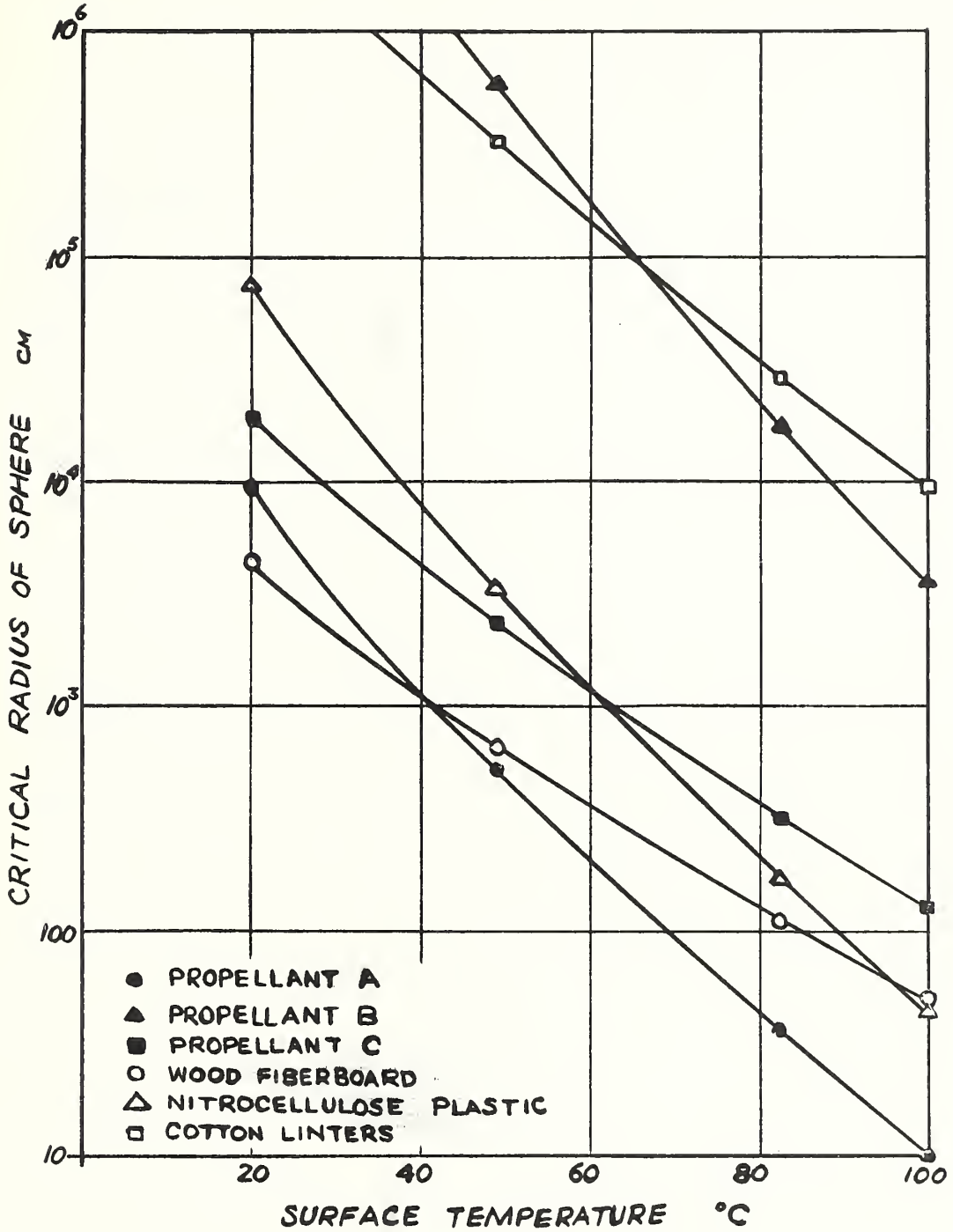
CRITICAL RADIUS OF SPHERE CM
10^6
10^5
10^4
100
10
20
40
60
80
100
SURFACE TEMPERATURE °C
PROPELLANT A
PROPELLANT B
PROPELLANT C
WOOD FIBERBOARD
NITROCELLULOSE PLASTIC
COTTON LINTERS

FIG. 5

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